

# PATENT SPECIFICATION

(11) 1322532

NO DRAWINGS

1322532

- (21) Application No. 24633/70 (22) Filed 21 May 1970  
 (21) Application No. 6131/71 (22) Filed 5 March 1971  
 (23) Complete Specification filed 19 May 1971  
 (44) Complete Specification published 4 July 1973  
 (51) International Classification C07C 131/00 B01D 15/04  
 (52) Index at acceptance



C2C 220 227 22Y 30Y 313 31Y 338 346 351 355 35Y  
 365 36Y 388 401 40Y 623 625 662 665 701 776  
 MV UQ

C1A D28 D45 G11 G11D28 G11D45 G13 G13D28  
 G13D45 G22 G22D28 G22D45 G9 G9D28 G9D45  
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## (54) HYDROXY-OXIMES AND THEIR USE IN THE EXTRACTION OF METAL VALUES

- (71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- The invention relates to a process for separation of metal values from aqueous media by liquid-liquid extraction employing certain hydroxy-oxime extractants, and, moreover, to novel hydroxy-oximes and the preparation thereof. More in particular, it relates to the selective extraction of copper values from aqueous media containing mixtures of copper and one or more other metal values.
- The term "metal values" as used in this Specification refers to compounds of metals other than alkali metals, notably to metal salts or ions derived therefrom; the relevant metal may or may not be present in a complex.
- Extractions of metal values from aqueous media are performed in numerous technical processes, for example, with the aim of isolating, or at least concentrating, one or more particular metal values from more or less dilute solutions. Other processes primarily aim at removing an undesired metal ion from the aqueous liquid. Selective extraction methods which allow the separation of different metal values are of particular importance in the mining industry, where the desired metal values often have to be recovered from aqueous solutions or suspensions of fairly complex mixtures of various metal salts. In such cases the starting materials usually originate from the leaching of ores, for example, with water, acids, bases or salt solutions, after the raw ores have been brought into a suitable form by crushing, grinding, sieving and/or flotation. After extraction, the metal values can be subjected to further treatments, such as stripping from the extract phase, precipitation, electrolysis and/or pyrometallurgical processes.
- It has already been proposed to extract copper from aqueous media by means of hydroxy-oxime extractants, viz., of a  $\alpha$ -hydroxyaliphatic ketone oximes or 2-hydroxybenzophenone oximes, for example 5,8-diethyl-7-hydroxydodecan-6-one oxime and 2-hydroxy-5-dodecylbenzophenone oxime, or mixtures thereof. It has been found that these known oximes possess certain disadvantages. The aliphatic  $\alpha$ -hydroxy-oximes, for example, require a relatively high pH, i.e. above 3—4, to acquire sufficient extractive capacity. A high pH, however, means a substantial alkali consumption when employing a strongly acidic aqueous medium as is usually obtained in copper leaching processes. The 2-hydroxybenzophenone oximes, on the other hand, are quite effective at lower pH's but the extraction times required are rather long. It has also been proposed to improve the extraction process by employing a mixture of aliphatic and aromatic ketone oximes.
- It has now been found that by modifying the structure of the ketone oximes, the above disadvantages may be obviated, i.e. the selective pH range can be very low and the extraction time is short. Moreover, in the present invention it is not necessary to employ a mixture of ketone oximes of different types to obtain good results.

Surprisingly, it has been found that highly efficient extractions are possible in a broad pH range which also covers very high acidities, e.g. a pH of from 0 to 2 (or even lower), when the extracting agent employed is a hydroxy-oxime as defined hereinbelow.

The present invention, therefore, relates to a process for the separation of metal values from an aqueous medium by liquid-liquid extraction, in which process the aqueous medium is contacted with an organic phase comprising an organic solvent, which is substantially immiscible with water, and—as an extracting agent—a hydroxy-oxime of the general formula  $A-C(=NOH)-R$ , in which R is an aliphatic group, and A represents a cyclic organic group carrying as substituents at least (a) hydroxyl group at a ring carbon atom which is in a 2-position (the number 1 being assigned to the ring carbon atom to which the  $-C(=NOH)-R$  group is attached), and (b) an organic group R', so as to extract at least a portion of the metal values into the organic phase, and—optionally—one or more metal values and/or metals are recovered from the organic phase after separation of the latter from the aqueous phase.

The extracting agent used has the aforementioned formula in which R is an aliphatic group, e.g. alkyl, alkenyl, alkapolyenyl and the like. The aliphatic group R may be branched or unbranched, and it may contain substituents and/or heteroatoms, if desired. An unbranched group has proved very favourable as a rule. The number of carbon atoms of the group R may range, for example, from 1 to 20, preferably from 5 to 20, and in particular from 7 to 11. An alkyl group is generally preferred. Examples of suitable alkyl groups are: methyl, ethyl, n-pentyl, n-heptyl, n-octyl, n-nonyl, n-undecyl, n-tridecyl and n-heptadecyl.

The symbol A in the above-mentioned general formula represents a cyclic organic group carrying the relevant substituents. The said cyclic group may be carbocyclic or heterocyclic, and it may optionally contain single or multiple double bonds. Examples are: cyclopentyl, cyclohexyl, cycloheptyl, phenyl, naphthyl and the like. Preference is given to an aromatic group, in particular to the phenyl group. As already mentioned, a hydroxyl group must be attached to a carbon atom being in a 2-position of the cyclic group, while—in addition—one or more organic groups R' are also present as substituents of the ring, e.g. alkyl, alkaryl, alkenyl, alkapolyenyl, alkoxy, alkylthio, alkoxy-carbonyl and the like. The relevant organic group (groups) may be branched or unbranched, and it (they) may contain substituents and/or heteroatoms, if desired. The number of carbon atoms of such a group R' may range, for example, from 1 to 20, preferably from 5 to 20, and in particular from 7 to 14. Preference is given to those compounds wherein R', or at least one of the groups R', represents an alkyl group, for example a secondary alkyl group. Examples of suitable alkyl groups are: methyl, sec-hexyl, sec-heptyl, sec-octyl, sec-nonyl, sec-undecyl and sec-pentadecyl. Preferably, not more than one substituent R' is present in the ring. Advantageously, the total number of carbon atoms present in the groups R and R' together amounts to at least 10 and not more than 25, a total of from about 14 to about 18 carbon atoms being particularly suitable. Preferably, the number of carbon atoms of the said groups R and R' is about the same.

Examples of very suitable hydroxy-oximes are: (5-sec-heptyl-2-hydroxyphenyl) n-heptylketone oxime; (5-sec-octyl-2-hydroxyphenyl) n-octyl ketone oxime; (5-sec-nonyl-2-hydroxyphenyl) n-nonyl ketone oxime; (5-sec-heptyl-2-hydroxyphenyl) n-nonyl ketone oxime. Further examples are: (2-hydroxy-5-methylphenyl) n-tridecyl ketone oxime; (2-hydroxy-5-sec-heptylphenyl) methyl ketone oxime; (2-hydroxy-5-sec-dodecylphenyl) ethyl ketone oxime; (2-hydroxy-5-sec-undecylphenyl) n-phenyl ketone oxime; (2-hydroxy-5-sec-hexylphenyl) n-undecyl ketone oxime; (2-hydroxy-5-sec-pentadecylphenyl) n-heptyl ketone oxime; (2-hydroxy-5-sec-octylphenyl) n-undecyl ketone oxime; (2-hydroxy-5-sec-octylphenyl) n-heptadecyl ketone oxime.

The hydroxy-oximes of the present invention are novel compounds. They have proved to be very efficient for the extraction of metal values from aqueous media in a wide pH range, generally down to a pH of about one. When, however, metal values are to be extracted from still more acidic media, i.e. of a pH lower than about 1, the efficiency of the extraction may often decrease considerably. Such highly acidic media may originate, for example, from a strongly acid leach of copper-containing ores. It should, moreover, be borne in mind that during the extraction with a hydroxy-oxime the pH of the aqueous phase decreases, owing to the formation of an equivalent amount of hydrogen ions. Maximum extraction of a desired metal value can, of course, be achieved even in the cases mentioned above, for example by allowing the extraction to proceed in a plurality of consecutive steps, or by addition of a base which raises the pH to an appropriate level.

Surprisingly, it has also been found that extractions with an excellent efficiency

are possible—even in a single step—in a broad pH range which covers, in particular, the regions of very high acidities, e.g. of a pH from 0 to 1 (or even lower), when the hydroxy-oxime of the general formula  $A-C(=NOH)-R$ , employed as the extracting agent, contains one or more electron-attracting substituents in the substituted cyclic group A, in addition to the other substituents already mentioned above.

Examples of such electron-attracting substituents are the halogen atoms, especially chlorine, bromine and fluorine, the nitro group, the cyano group, and an alkoxy-carbonyl group  $CO_2R''$ , in which  $R''$  is an alkyl group having from 1 to 20 carbon atoms, such as—preferably—a methoxycarbonyl or an ethoxycarbonyl group. As the electron-attracting substituent a halogen atom is usually preferred, particularly chlorine. Excellent results have been obtained with compounds containing only one electron-attracting substituent in the ring. Optionally, however, two or more of such substituents may be present which may be similar or dissimilar to each other. The said substituents are particularly effective when the cyclic organic group, to which they are attached, is of an aromatic character, especially when it is a phenyl group.

Thus, according to a preferred embodiment of the invention the substituted cyclic group A carries as substituents those mentioned above, viz., a hydroxyl group, an organic group  $R'$  and possibly an electron-attracting substituent. When, the said electron-attracting substituent at the same time represents such an organic group  $R'$ , as may be the case with, for example, an alkoxy-carbonyl group, an additional group  $R'$  need not necessarily be present as well. In these cases it is usually desirable that the total number of carbon atoms of one or more of these electron-attracting substituents, of the aliphatic group R, and of any additional groups  $R'$ —if present—together ranges from 10 to 25, and in particular from 14 to 18.

Favourable positions of the electron-attracting substituent, or substituents in the ring are, in general, those where the said substituent, or substituents, will induce an increased acidity of the hydroxyl group present in a 2-position. Accordingly, when the ring is a phenyl group, the 3- and/or 5-positions are most preferred, the 2-position being occupied by a hydroxyl group. Thus, excellent results have been obtained, for example, with the relevant 3-chloro-2-hydroxyphenyl derivatives. The organic group, or groups,  $R'$  may, as a rule, occupy any of the remaining positions of the cyclic group. Suitable compounds are, for example, those having a group  $R'$ —preferably an alkyl group—in the 5-position of a phenyl group.

Thus further examples of very suitable extracting agents, according to this invention, are hydroxy-oximes of the general formula  $A-C(=NOH)-R$  wherein A and R each represent one of the following groups:

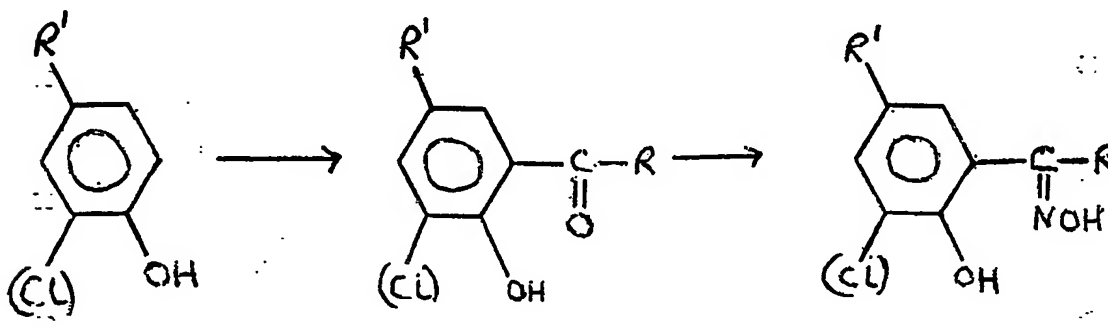
	A	R	
	5-sec-heptyl-3-chloro-2-hydroxyphenyl	n-heptyl	
	5-sec-octyl-3-chloro-2-hydroxyphenyl	n-octyl	
40	5-sec-nonyl-3-chloro-2-hydroxyphenyl	n-nonyl	40
	5-sec-heptyl-3-chloro-2-hydroxyphenyl	n-nonyl	
	5-sec-octyl-3-chloro-2-hydroxyphenyl	n-nonyl	
	5-methyl-3-chloro-2-hydroxyphenyl	n-tridecyl	
	5-sec-heptyl-3-chloro-2-hydroxyphenyl	methyl	
45	5-sec-dodecyl-3-chloro-2-hydroxyphenyl	ethyl	45
	5-sec-undecyl-3-chloro-2-hydroxyphenyl	n-pentyl	
	5-sec-hexyl-3-chloro-2-hydroxyphenyl	n-undecyl	
	5-sec-pentadecyl-3-chloro-2-hydroxyphenyl	n-heptyl	
	5-sec-octyl-3-chloro-2-hydroxyphenyl	n-undecyl	
50	5-sec-octyl-3-chloro-2-hydroxyphenyl	n-heptadecyl	50

Excellent results have been obtained, in particular, with (5-sec-octyl-3-chloro-2-hydroxyphenyl) n-nonyl ketone oxime.

The extracting agents of the present invention, which are all novel compounds, may, of course, also be used as mixtures of two or more of the relevant hydroxy-oximes and/or together with other suitable extracting agents, e.g. with other hydroxy-oximes.

The hydroxy-oximes can readily be synthesized, for example, by oximation of the corresponding ketones by any known process. The oximation of the ketones may be carried out by reacting the ketones with a hydroxylamine salts. Convenient routes for the preparation of hydroxy-oximes having a substituted phenyl group A preferably involve the condensation of an alkylphenol—optionally containing an electron-attracting substituent such as chlorine in the nucleus—with an acyl chloride,  $R-COCl$ , or with a trichloroalkane,  $R-CCl_3$ , in the presence of  $AlCl_3$ , in the latter case followed by hydrolysis, or with a carboxylic acid,  $R-CO_2H$ , in the presence of  $BF_3$ , and subse-

quent oximation of the resulting ketone. Suitable starting materials are the appropriate 4-alkyl-phenols—usually obtained by alkylation of phenol with an alpha-olefin—which may, if required, be chlorinated in the 2-position prior to acylation. The corresponding hydroxy-oximes may be prepared, for example, according to the following reaction scheme:



Optionally, however, the halogenation can be carried out at a latter stage, e.g. in the ketone prior to oximation. Examples of commercially available 4-alkylphenols, which may be used in these syntheses are, inter alia, 4-heptylphenol, 4-octylphenol and 4-nonylphenol.

The oximation of the relevant alkyl phenyl ketones may be carried out by reacting the alkyl phenyl ketone with a hydroxylamine salt under reflux conditions comprising refluxing the reactants in e.g. an alcohol, such as ethanol, in the presence of a base, e.g. pyridine, to combine with the acid associated with the hydroxylamine. It is preferred to use an excess of the hydroxylamine salt, which may be the hydrochloride, the hydrogen sulphate, or the like.

The special method of manufacture which may be used for the preparation of the extracting agent is dependent on the special compounds which are used as starting material, and the effectiveness of the special method applied to such starting materials.

For the selective extraction according to the invention the hydroxy-oximes of the above formula are generally used in a dilute form in a water-immiscible organic solvent. It is to be recommended that the water-immiscible organic solvent be so chosen that the organic phase does not dissolve in the aqueous medium, and vice-versa, or only to a slight extent. The mutual miscibility of the phases should preferably not exceed 5%v, and in particular be lower than 1%v. Suitable solvents are, for example, halogenated solvents, such as chloroform, 1,2-dichloroethane, 1,2-dichloropropane and di-(2-chloroethyl)ether, and in particular hydrocarbons, e.g. kerosene, toluene and the xylenes.

The organic phase may also contain other materials, such as a conditioner, which is usually a long-chain aliphatic alcohol, for preventing or demulsifying emulsions which could have been formed during extraction of the aqueous medium in the course of which vigorous stirring is recommended to ensure a good contact between the two phases.

The process of this invention is very suitable for the extraction of one or more metal values, such as copper, iron, nickel, cobalt and/or other metal values, and it is of particular value for the selective extraction from solutions containing two or more metal values. The starting materials for the extraction often originate, for example, from the leaching of ores, e.g. with acids, or with a base such as ammonia (under pressure), after the raw ores have been brought into a suitable form.

While the hydroxy-oximes of this invention are particularly useful for the extraction of metal values from highly acidic media, they are usually effective in a wide pH range also covering the basic media, depending on the metal value (values) to be separated and on other metal values which may also be present in the aqueous phase. Thus, when copper(II) values are to be separated from iron(III) and/or other metal values, such as nickel and cobalt, the regions of low pH are preferred, especially a pH of from zero to two, whereas nickel(II) values are selectively extracted from cobalt(III) values preferably from an aqueous ammoniacal medium, after oxidation—if necessary—of the cobalt values to the trivalent state, e.g. by means of oxygen or an oxygen-containing gas—preferably air—, which leaves the nickel values in the divalent state.

The optimum pH for the selective extraction of a certain metal value depends, inter alia, on the nature of the relevant metal, and of course also on the extracting agent used. However, the other metal value (values) present in the aqueous phase should also be taken into account. For example, to prevent co-extraction of one or more undesired metal values, it may often be advisable to choose a lower pH than that preferred in the absence of such other metal values, even if maximum extraction is not achieved in a single step. In such cases it is profitable to carry out the process at such a non-optimum pH and effecting the extraction in a plurality of consecutive steps, use being preferably made of a continuous process and/or the counter-current principle. In most cases complete separations can readily be achieved in this manner.

For successfully effecting the selective extraction of copper values according to the process of the present invention the aqueous medium, such as a solution resulting from the leaching of ores, should preferably have a pH value not greater than 2.0, the range of pH 0.0 to 1.5 being especially preferred. It should be noted in this connection that those hydroxy-oximes having an electron-attracting substituent in the cyclic group A are, as a rule, particularly effective in a pH range of from 0.0 to 0.8, while the other hydroxy-oximes of the present invention are very advantageously applied at a somewhat higher pH, preferably in the range of from 1 to 1.5. In the said pH ranges, it has unexpectedly been found that from aqueous media containing both iron and copper values, the copper may readily be extracted while the iron remains in the aqueous medium. If necessary, the aqueous solutions resulting from the leaching procedure may be brought to the desired pH by addition of an acid for instance sulphuric acid.

The process of the present invention is particularly useful for the separation of Cu, Fe and Co and/or Ni values, and especially for the extraction of Cu(II) from a medium that also contains Fe(III). The concentrations of the metal values in the aqueous medium may vary between wide limits, and are usually between 0.01 and 1 mole/litre, and preferably between 0.05 and 0.5 mole/litre.

The selective extraction according to the invention is preferably carried out in a continuous manner. It may readily be carried out by bringing the aqueous medium—for instance after the addition of a mineral acid, e.g.  $H_2SO_4$ —into contact with a solution of the hydroxy-oxime in e.g. kerosene. It is advisable that contact between the phases be promoted by vigorous stirring. Stirring is preferably continued until equilibrium between the phases has been established, which is generally the case after 1 to 5 minutes. A favourable volume ratio of the organic phase to the aqueous medium has been found to be 1:3 to 3:1. However, other ratios may also be used. As a rule, the extraction proceeds smoothly at room temperature. However, higher or lower temperatures are not excluded.

Adjustment of the aqueous medium to the required pH during the extraction, if necessary, may be brought about by addition of an acid or a base, such as sulphuric acid, hydrochloric acid, an alkali metal hydroxide or carbonate, or by means of ammonium hydroxide, the technique particularly preferred being gradual and continuous addition of the acid or base while the mixture is contacted with the extracting agent. Adjustment of the pH and extraction are thus carried out simultaneously.

The extracted metal value(value)s may advantageously be recovered from the organic phase—which is usually a solution of a complex of the hydroxy-oxime used and the relevant metal in a suitable solvent, such as kerosene—by stripping with an aqueous solution of a strong acid, preferably sulphuric or nitric acid, after separation of the organic phase from the aqueous phase. The organic phase can also be stripped by alternately contacting said phase with an aqueous solution containing an acid and with water. The metal value (values), e.g. copper, are thus transferred to the aqueous stripping medium as the corresponding metal salts, e.g. as sulphates, and can then be recovered by conventional techniques, for example as salts, by evaporation of the water and/or crystallization, or as metals by direct electrolysis, while the organic phase containing the released extracting agent is advantageously used again for subsequent extractions. Often, however, it may be desirable to use a base, such as ammonia, for the stripping operation. For, in many cases, the desired value, e.g. nickel, can then be precipitated by evaporation of the ammonia.

Since the concentration of, for example, copper in the extract phase can be varied simply by varying the volume ratio of the organic and aqueous phases, any problem of low copper concentration in the original copper containing aqueous solutions is obviated. Inasmuch as the copper can be stripped from the loaded organic phase by strong acids into a small volume of aqueous stripping medium, a further concentration of copper values can be effected.

Metal values, such as copper, may readily be recovered in the form of their salts. Thus, when sulphuric acid is used as the stripping solution, copper sulphate can be

crystallized from the copper-pregnant stripping solution. Preferably, the volume of the stripping medium is kept low and usually warmer than ambient room temperature so as to obtain a pregnant solution high in copper values. The copper salt then crystallizes out in the stripping stage(s) if a high enough concentration is obtained. It may also be crystallized apart from the organic phase by cooling to ambient temperature or below. Additionally, such salts can be recovered by evaporation of the stripping solution. Copper salts such as copper sulfate are valuable products and can be obtained in high purity by this process.

In carrying out the process of the invention, both the extraction and stripping operations may be performed batchwise, in a single stage or in a number of consecutive stages, or, preferably, in a continuous manner, for example by employing co-current or counter-current techniques.

In both cases it may be convenient to recover a metal value direct from the loaded organic phase by hydrogenation of the latter, which often allows the relevant metal to be obtained in the form of a powder.

The process of the invention may in general be employed, for example, for the isolation, or at least concentration, of one or more particular metal values from more or less dilute solutions, or for the removal of an undesired metal value from an aqueous medium, and it is of particular value for the separation of different metal values from one another, which may occur as solutions or suspensions of fairly complex mixtures of various metal salts.

#### EXAMPLE I

Preparation of (2-hydroxy-5-methylphenyl) n-tridecyl ketone oxime

228 grams (1 mole) of myristic acid and 238 grams (2 moles) of thionyl chloride were combined in a 2 litre threenecked flask equipped with a thermometer, stirrer and reflux condenser. The mixture was during stirring slowly warmed up and thereafter heated for 2½ hours. Then excess of thionyl chloride was removed in vacuum. After distilling the residue 246.5 grams (1 mole) myristic acid chloride was obtained, which was dropwise added to another 2 l three-necked flask provided also with a thermometer, stirrer and reflux condenser containing 108 grams (1 mole) of *p*-cresol. The mixture was stirred at a temperature of 80°C till HCl generation ceased. Then the above mixture was poured out into water and stirred at a temperature of 80°C. The organic layer was extracted with diethylether and successively washed with water, an aqueous solution of NaHCO<sub>3</sub> and at last again with water and finally dried over sodium sulfate. Removal of the ether under vacuum gave 302 gram of the impure *p*-cresyl ester of myristic acid, which was further used without any purification. Together with 140 grams (1.05 moles) of aluminium chloride the whole quantity of the above ester was added to a 2 l threenecked flask, equipped in the same way as already mentioned before. The temperature was raised to 90–115°C and the mixture was stirred till foaming had ceased, after which stirring was continued for about 2½ hours. The warm mixture was then poured out into an excess of 6 n HCl. After extraction with diethylether and successively washing the product with water, an aqueous solution of NaHCO<sub>3</sub> and again with water and finally drying the product over sodium sulfate, 283 grams of a colourless crystallized 2-myristoyl-5-methylphenol was obtained which had a melting point of 56.8–57.1°C. Finally, 270.3 grams (0.85 mole) of the above ketophenol, 70.9 grams (1.02 moles) of hydroxylamine hydrochloride and 312 grams (3 moles) of sodium acetate 3 aq. and 1 l ethylalcohol were added to a 2 l three-necked flask equipped in the usual manner and heated for 4 hours. After expulsion of the alcohol on a vapour bath the residue was taken up in diethyl ether and successively washed with water, an aqueous solution of NaHCO<sub>3</sub> and again with water and finally dried over sodium sulfate. After removal of the ether 310 grams of umpure (2-hydroxy-5-methylphenyl) n-tridecyl ketone oxime was obtained which proved to be polluted with 2–3% of the starting ketophenol. Crystallization of this oxime from an ether/alcohol mixture gave a water white crystallized product that had a melting point of 98.5–100.3°C, a very good solubility in ether and kerosine and moderate solubility in ethylalcohol.

#### EXAMPLE II

Preparation of (2-hydroxy-5-sec-dodecylphenyl)ethyl ketone oxime

92.5 grams (1 mole) of propionyl chloride and 262 grams (1 mole) of *p*-sec-dodecylphenol (obtained by alkylation of phenol with propylene tetramer) were combined in a 2 l three-necked flask equipped with a thermometer, stirrer and reflux condenser. The mixture was during stirring slowly warmed up and thereafter heated for at least 1 hour. Then the mixture was poured out into water and stirred at 60°C to break up excess of propionylchloride. After extraction with pentane the residual mix-

ture was successively washed with water, an aqueous solution of  $\text{NaHCO}_3$ , and again with water and finally dried over sodium sulfate. At last the pentane was removed by evaporation and 298.4 grams of the impure p-dodecylphenyl propionate was obtained. Together with 140 grams (1.05 moles) of aluminium chloride, the whole quantity of the above propionate was added to a 2 l three-necked flask equipped in the usual way. The temperature was slowly raised till foaming had ceased. At a temperature of  $120^\circ\text{C}$  the mixture was stirred for about 1 hour. Then the warm mixture was poured out into an excess of 6 n HCl and subsequently extracted with diethylether. The ether layer was successively washed with water, an aqueous solution of  $\text{NaHCO}_3$ , and again with water and finally dried over sodium sulfate, after which 308.4 grams of impure (2-hydroxy-5-sec-dodecylphenyl) ethyl ketone was obtained.

298.9 grams (0.94 mole) of the above ketone, 70.9 grams (1.02 moles) of hydroxylamine hydrochloride, 312 grams (3 moles) of sodium acetate 3 aq. and 1 l ethylalcohol were added to a 2 l threenecked flask equipped in the usual way. After heating for about 3 hours and expulsion of the alcohol in a vapour-bath the residue was taken up in diethylether, successively washed with water, an aqueous solution of  $\text{NaHCO}_3$ , and again with water and finally dried over sodium sulfate. Removal of the ether by evaporation in vacuum gave 333 grams (1 mole) of impure (2-hydroxy-5-sec-dodecylphenyl) ethyl ketone oxime, which was readily soluble in kerosene and may be used without any purification as a copper extracting agent.

### EXAMPLE III

In a manner similar to the one described in Example I the following compounds were synthesized:

(2-hydroxy-5-sec-heptylphenyl) methyl ketone oxime;  
 (2-hydroxy-5-sec-heptylphenyl) n-heptyl ketone oxime;  
 (2-hydroxy-5-sec-octylphenyl) n-octyl ketone oxime;  
 (2-hydroxy-5-sec-undecylphenyl) n-pentyl ketone oxime;  
 (2-hydroxy-5-sec-hexylphenyl) n-undecyl ketone oxime;  
 (2-hydroxy-5-sec-pentadecylphenyl) n-heptyl ketone oxime;  
 (2-hydroxy-5-sec-octylphenyl) n-undecyl ketone oxime;  
 (2-hydroxy-5-sec-octylphenyl) n-heptadecyl ketone oxime;  
 (2-hydroxy-5-sec-nonylphenyl)n-nonyl ketone oxime;  
 (2-hydroxy-5-sec-heptylphenyl) n-nonyl ketone oxime.

### EXAMPLE IV

Preparation of 5-sec-octyl-3-chloro-2-hydroxyphenyl) n-nonyl ketone oxime. 490 Grams (2.36 mole) of 4-sec-octylphenol (available as "octylphenol" from, e.g., Ketjen NV and I.C.I. Ltd.) was dissolved in 1.5 litres of chloroform, and 53 litres (2.37 mole) of gaseous  $\text{Cl}_2$  was then introduced at a temperature of  $-15^\circ\text{C}$  to  $-10^\circ\text{C}$  at a rate of 20 l/h. The mixture was allowed to stand overnight, whereupon the chloroform was removed by evaporation. This afforded 564 grams (2.34 mole) of 4-sec-octyl-2-chlorophenol. (I); yield, 98.7%.

430 Grams (2.5 mole) of n-decanoic acid was refluxed for 4 hours with 950 grams (8 mole) of thionyl chloride. After removal of the excess of thionyl chloride in vacuo, 456 grams (2.5 mole) of crude n-decanoyl chloride (II) was obtained; yield 100%.

The whole of product I was heated to  $80^\circ\text{C}$  in a three-necked vessel provided with stirrer, reflux condenser and dropping funnel, and 450 grams (2.48 mole) of product II was then added dropwise with stirring over a period of 1.5 h. Heating at  $80^\circ$  was continued until no more HCl evolved, and subsequently for one more hour. The mixture was then poured into water and heated to  $80^\circ\text{C}$  for 1 hour. After cooling, the mixture was extracted with ether, the ether layer washed with water, sodium bicarbonate solution, and again water. After drying over  $\text{Na}_2\text{SO}_4$ , the ether was removed in vacuo. This gave 840 grams (2.13 mole) of crude 4-sec-octyl-2-chlorophenyl ester of n-decanoic acid; yield 91%.

This product was heated with 314 grams (2.35 mole) of  $\text{AlCl}_3$  for 49 hours at  $80^\circ\text{C}$  and for another 10 hours at  $105^\circ\text{C}$ . The still warm mixture was poured into an excess of a 50/50 (v/v) mixture of concentrated aqueous HCl and water and heated at  $80^\circ\text{C}$  to completely decompose the complex formed. The oily layer was extracted with ether, washed repeatedly with water and sodium bicarbonate solution, dried over  $\text{Na}_2\text{SO}_4$ , and the ether removed in vacuo to give 630 grams (1.6 mole) of crude 5-sec-octyl-3-chloro-2-hydroxyphenyl)n-nonyl ketone; yield 75%.

This ketone was finally oximated by refluxing for 72 hours in 100% ethanol together with 140 g (2 mole)  $\text{NH}_2\text{OH}$ . HCl and 390 grams (4 g mole) sodium acetate.



The ethanol was removed by evaporation, the residue taken up in ether and the ether layer washed and dried over  $\text{Na}_2\text{SO}_4$ . After evaporation of the ether 591 grams (1.45 mole) (5-sec-octyl-3-chloro-2-hydroxyphenyl) n-nonyl ketone oxime was obtained; yield 90.5%.

#### EXAMPLE V

The extraction experiments were conducted in a specially designed separatory funnel consisting of a graduated, straight-walled vessel with a capacity of 0.25 litre. At the bottom a stopcock was provided for draining the funnel. The top opening was used to introduce the double-paddle stirrer, and it also served as the inlet for the feed. The extractions were carried out by contacting 50 ml of an aqueous solution containing metal value(s) with 100 ml of the organic extraction solution, and stirring at a rate of about 2000 rpm.

Selective extraction of  $\text{Cu}^{2+}$  with (2-hydroxy-5-sec-octylphenyl) n-octyl ketone oxime.

The aqueous feed used was a solution containing 3.18 g  $\text{Cu}^{2+}$  and 2.79 g  $\text{Fe}^{3+}$  per litre in the form of their sulphates and, in addition, 20 g  $\text{H}_2\text{SO}_4$  per litre. This feed has a pH of 0.0. The solution was then contacted with a 0.5 m solution of the hydroxy-oxime in kerosene, the volume ratio of organic phase/aqueous phase being 2:1. During vigorous stirring at room temperature neutralization was effected by addition of 25%w aqueous ammonia at a rate of 0.1 ml per minute. At various intervals addition of ammonia was interrupted.

After stirring for another two minutes, the phases were separated and the pH of the aqueous phase was determined. The organic phase was subsequently regenerated by back-washing with 2 N  $\text{H}_2\text{SO}_4$ , the copper and iron values being estimated in the aqueous phase obtained.

The respective amounts of copper extracted at different pH levels which are defined at being the pH of the aqueous solution in equilibrium with the corresponding organic phase, are shown in Table I below together with the amount of co-extracted iron at the same pH level.

TABLE I

Experiment	pH	%w extracted (cumulative)	
		$\text{Cu}^{++}$	$\text{Fe}^{+++}$
1	0.20	12.1	2.2
2	0.55	33.6	4.7
3	0.90	63.3	7.1
4	1.25	89.5	10.4
5	1.55	98.9	15.5
6	1.85	100.0	24.2
7	2.25	100.0	43.8

#### EXAMPLE VI

Extraction of  $\text{Cu}^{2+}$  with (2-hydroxy-5-sec.dodecylphenyl)-ethyl ketone oxime.

In each experiment 50 ml of a copper sulfate solution (0.05 m Cu) (which has a pH of 0.7) was stirred with 100 ml 0.5 m of a solution of (2-hydroxy-5-sec-dodecylphenyl) ethyl ketone oxime in kerosene. Meanwhile pH adjustment was effected by addition of 25%w aqueous ammonia with a velocity of 0.1 ml/minute. After that stirring was continued for 2 minutes. Subsequently, when separation in an organic layer and a water layer had occurred, the pH of the water layer was measured. Then in the organic layer which was stripped back with 100 ml of 2 n  $\text{H}_2\text{SO}_4$ , the copper content was determined.

TABLE II

Experiment	pH	Cu %w extracted (cumulative)
1	0.32	12.9
2	0.60	41.2
3	1.04	73.8
4	1.32	97.3
5	2.14	100

It is seen from Table II above that hydroxy-oximes of the present invention are very efficient copper extractants down to a pH of at least 1.04 and somewhat below. This is the pH that is of interest for the extraction of copper from ore leach liquors.



## EXAMPLE VII

Selective extraction of  $\text{Cu}^{2+}$  with (5-sec-octyl-3-chloro-2-hydroxyphenyl) n-nonyl ketone oxime.

The aqueous feed used was a solution containing 3.18 g  $\text{Cu}^{2+}$  and 2.79 g  $\text{Fe}^{3+}$  per litre in the form of their sulphates and, in addition, 20 g  $\text{H}_2\text{SO}_4$  per litre. This feed had a pH of 0.0. The solution was contacted with a 0.5 M solution of the hydroxy-oxime in kerosene, the volume ratio of organic phase/aqueous phase being 1:1. During vigorous stirring at room temperature neutralisation was effected by addition of predetermined amounts of 25%w aq.  $\text{NH}_3$  at a rate of 0.1 ml/min.

After stirring for another two minutes, the phase were separated and the pH of the aqueous phase was determined. The organic phase was subsequently regenerated by back-washing with 2-N  $\text{H}_2\text{SO}_4$ , the copper and iron values being estimated by atomic absorption measurements of the aqueous phase obtained.

The respective amounts of copper extracted at different pH levels which are defined as being the pH of the aqueous solution in equilibrium with the corresponding organic phase, are shown in Table III below together with the amount of iron co-extracted at the same pH level.

TABLE III

experiment	pH	%w extracted (cumulative)	
		$\text{Cu}^{2+}$	$\text{Fe}^{3+}$
1	0.06	59.1	4.9
2	0.21	90.9	5.4
3	0.56	95.9	6.1
4	0.77	96.8	7.3

## EXAMPLE VIII

Extraction of  $\text{Cu}^{2+}$  with (5-sec-octyl-3-chloro-2-hydroxyphenyl) n-nonyl ketone oxime.

An aqueous solution containing 3.18 g  $\text{Cu}^{2+}$  per litre as the sulphate and 20 g  $\text{H}_2\text{SO}_4$  per litre was extracted with 0.5 kerosene solution of the hydroxy-oxime. The operation was carried out in a manner analogous to that described in Example VII above. The following results were obtained (see table IV).

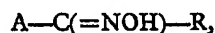
TABLE IV

experiment	pH	%w $\text{Cu}^{2+}$ extracted (cumulative)
1	0	72.8
2	0.05	82.8
3	0.12	90.9
4	0.20	97.0
5	0.35	100

The results show that very efficient extractions of copper values are achieved down to a pH of 0. Higher acidities are, of course, also possible.

## WHAT WE CLAIM IS:—

1. A process for the separation of metal values from an aqueous medium by liquid-liquid extraction, in which process the aqueous medium is contacted with an organic phase comprising an organic solvent, which is substantially immiscible with water, and—as an extracting agent—a hydroxy-oxime of the general formula



in which R is an aliphatic group, and A represents a cyclic organic group carrying as substituents at least (a) a hydroxyl group at a ring carbon atom which is in a 2-position (the number 1 being assigned to the ring carbon atom to which the  $-\text{C}(=\text{NOH})-\text{R}$  group is attached), and (b) an organic group  $\text{R}'$ , so as to extract at least a portion of the metal values into the organic phase, and—optionally—one or more metal values and/or metals are recovered from the organic phase after separation of the latter from the aqueous phase.

2. A process as claimed in claim 1, in which the aliphatic group R is an alkyl group.

3. A process as claimed in claim 2, in which the alkyl group R is unbranched.

4. A process as claimed in any one of claims 1—3, in which the aliphatic group R contains 5 to 20 carbon atoms.
5. A process as claimed in claim 4, in which the group R contains 7 to 11 carbon atoms.
- 5 6. A process as claimed in any one of claims 1—5, in which the substituted cyclic group A is a substituted phenyl group.
7. A process as claimed in any one of claims 1—6, in which the organic substituent R', or at least one such substituent, contains 5 to 20 carbon atoms.
- 10 8. A process as claimed in claim 7, in which the substituent R' contains 7 to 14 carbon atoms.
9. A process as claimed in any one of claims 1—8, in which the organic substituent R', or at least one such substituent, is an alkyl group.
10. A process as claimed in any one of claims 1—9, in which the substituted cyclic group A contains not more than one substituent R'.
- 15 11. A process as claimed in any one of claims 1—10, in which the group A is a 2-hydroxy-5-alkylphenyl group.
12. A process as claimed in any one of claims 1—11, in which the group A contains, in addition, one or more electron-attracting substituents.
- 20 13. A process as claimed in claim 12, in which the electron-attracting substituent, or at least one such substituent, is a halogen atom.
14. A process as claimed in claim 13, in which the halogen atom is a chlorine atom.
15. A process as claimed in any one of claims 12—14, in which the group A contains not more than one electron-attracting substituent.
- 25 16. A process as claimed in any one of claims 1—15, in which the total number of carbon atoms of the groups R and R', and of the electron-attracting substituent (substituents)—if present—, together ranges from 10 to 25.
17. A process as claimed in claim 16, in which the total number of carbon atoms of the said groups, and of the said substituent (substituents), together ranges from 14 to 18.
- 30 18. A process as claimed in any one of claims 1—10 and 17, in which the hydroxy-oxime is (2-hydroxy-5-sec-octylphenyl) n-octyl ketone oxime.
19. A process as claimed in any one of claims 12—17, in which the group A is 5-alkyl-3-chloro-2-hydroxyphenyl group.
- 35 20. A process as claimed in any one of claims 12—17 and 19, in which the hydroxy-oxime is (5-sec-octyl-3-chloro-2-hydroxyphenyl) n-nonyl ketone oxime.
21. A process as claimed in any one of claims 1—20, in which the solvent is so chosen that the mutual miscibility of the organic and aqueous phases does not exceed 5%v.
- 40 22. A process as claimed in any one of claims 1—21, in which the solvent used is kerosene, toluene or the xylenes.
23. A process as claimed in any one of claims 1—22, in which the contact between the organic and aqueous phases during the extraction is promoted by vigorous stirring until equilibrium between the phases has been established.
- 45 24. A process as claimed in any one of claims 1—23, in which the aqueous metal subjected to the extraction is a leach liquor resulting from the leaching of ores.
25. A process as claimed in any one of claims 1—24, in which one or more metal values are extracted from an aqueous medium comprising copper, iron, nickel and/or cobalt values.
- 50 26. A process as claimed in any one of claims 1—25, in which the concentration of the metal value to be extracted is between 0.01 and 1 mole/litre.
27. A process as claimed in any one of claims 1—26, in which the volume ratio of the organic phase to the aqueous medium is in the range from 1:3 and 3:1.
28. A process as claimed in any one of claims 1—27, in which copper values are extracted.
- 55 29. A process as claimed in any one of claims 1—28, in which copper(II) values are selectively extracted from an aqueous medium which also contains iron(III).
30. A process as claimed in any one of claims 1—29, in which the extraction of copper values is carried out at a pH ranging from 0.0 to 2.0.
- 60 31. A process as claimed in any one of claims 1—11, 16—18, and 21—30, in which the extraction of copper values is carried out at a pH ranging from 1 to 1.5.
32. A process as claimed in any one of claims 1—10, 12—17, and 19—30, in which the extraction of copper values is carried out at a pH ranging from 0.0 to 0.8.
33. A process as claimed in any one of claims 1—32, in which the aqueous medium is adjusted to the required pH during the extraction by gradual and continuous addition of a base, to the mixture.
- 65

34. A process as claimed in any one of claims 1—27, in which nickel(II) values are selectively extracted from Co(III) values from an aqueous ammoniacal medium.

35. A process as claimed in any one of claims 1—34, in which the extracted metal value (values) are recovered from the organic extract phase after separation of the latter from the aqueous phase.

36. A process as claimed in claim 35, in which the extracted metal value (values) is (are) stripped from the organic phase with an aqueous solution of a strong acid.

37. A process as claimed in claim 36, in which sulphuric acid or nitric acid is used in the stripping operation.

38. A process as claimed in any one of claims 35—37, in which the organic phase, containing the hydroxy-oxime liberated in recovering the metal value (values) from the extract phase, is used again in a subsequent extraction.

39. A process as claimed in any one of claims 1—38, in which the extraction and/or the stripping operations are performed in a continuous manner.

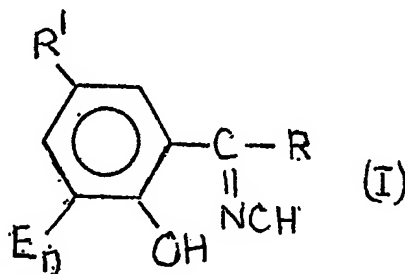
40. A process as claimed in any one of claims 1—39, substantially as hereinbefore described, with special reference to Examples V—VIII.

41. A metal value or metal values, whenever obtained by a process claimed in any one of claims 1—40.

42. Hydroxy-oximes of the general formula  $A-C(=NOH)-R$  as defined in any one of claims 1—20.

43. Hydroxy-oximes as claimed in claim 42, in which R is an alkyl group, and A represents a 2-hydroxyphenyl group carrying at least one alkyl substituent R' and—optionally—one or more electron-attracting substituents in the phenyl nucleus.

44. Hydroxy-oximes of the general formula



in which both R and R' are alkyl groups having from 5 to 20 carbon atoms each; E represents an electron-attracting substituent, and n=zero or 1.

45. Hydroxy-oximes as claimed in claim 43 or 44, in which the alkyl group R contains 7 to 11 carbon atoms.

46. Hydroxy-oximes as claimed in any one of claims 43—45, in which the alkyl substituent R' contains 7 to 14 carbon atoms.

47. Hydroxy-oximes as claimed in any one of claims 43—46, in which R and R' together contain 10 to 25 carbon atoms.

48. Hydroxy-oximes as claimed in claim 47, in which R and R' together contain 14 to 18 carbon atoms.

49. Hydroxy-oximes as claimed in any one of claims 43—48, in which an electron-attracting substituent E is present in the phenyl nucleus (n=1).

50. Hydroxy-oximes as claimed in claim 49, in which E is a chlorine atom.

51. (2-Hydroxy-5-methylphenyl) n-tridecyl ketone oxime.

52. (2-Hydroxy-5-sec-dodecylphenyl) ethyl ketone oxime.

53. (2-Hydroxy-5-sec-octylphenyl) n-octyl ketone oxime.

54. (5-Sec-octyl-3-chloro-2-hydroxyphenyl) n-nonyl ketone oxime.

55. The (2-hydroxy-5-alkylphenyl) n-alkyl ketone oximes listed in Example III.

56. A process for the preparation of hydroxy-oximes as defined in any one of claims 43—55, in which the appropriate 4-alkylphenol—which optionally contains an electron-attracting substituent in the phenyl nucleus—is reacted with an acyl chloride,  $R-COCl$ , or with a trichloroalkane,  $R-CCl_3$ , in the presence of  $AlCl_3$ , in the latter

case followed by hydrolysis, or with a carboxylic acid,  $R-CO_2H$ , in the presence of  $BF_3$ , and the resulting ketone is converted into the corresponding oxime by any known process.

5 57. A process as claimed in claim 56, substantially as hereinbefore described, with special reference to Examples I—IV.

58. Hydroxy-oximes whenever obtained by a process as claimed in claim 56 or 57. 5

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Printed for Her Majesty's Stationary Office, by the Courier Press, Leamington Spa, 1973.  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.